

"Express Mail" mailing label number EV 339772715US
Date of Deposit: September 8, 2003

Our Case No. 10908/5
Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR UNITED STATES LETTERS PATENT

INVENTORS:	Noelene Ahern Jozef Marie Schaekers
TITLE:	RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS
ATTORNEY:	G. Peter Nichols BRINKS HOFER GILSON & LIONE P.O. BOX 10395 CHICAGO, ILLINOIS 60610 (312) 321-4200

RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS

[0001] The present application is a continuation of and claims priority to PCT/ZA02/00024 filed March 6, 2002, which was published in English on September 12, 2002, and which claims priority to South African Patent Application No. 2001/1927 filed March 8, 2001, the entire contents of both are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

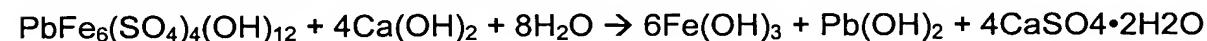
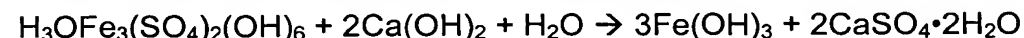
[0002] This invention relates to the recovery of metals from jarosite-containing materials.

[0003] The leaching of certain metals e.g. silver (Ag), lead (Pb) and zinc (Zn) using brine leaching, is well known.^(1,2,3,4,5) The ease of solubilising these metals depends on the refractory nature of the material treated.

[0004] To improve recoveries from refractory materials by brine leaching, a combined high temperature oxidation process in combination with acidic brine leaching has been proposed.⁽⁴⁾ A concentrate containing silver, mostly in sulfide minerals, yielded only 50% Ag dissolution in a FeCl₃ brine leach. By leaching the concentrate at temperatures above 100°C with a high oxygen partial pressure in an acidic NaCl or CaCl₂ medium, the Ag recovery was increased to above 95%.

[0005] Brine leaching alone is not effective in solubilising metals included in or encapsulated by jarosite or other similar iron hydroxy sulfate compounds since these compounds must first be decomposed.

[0006] Decomposition of jarosites in alkaline media is well known. Jarosites produced during pressure leaching of zinc concentrates were decomposed by treating the residues with a lime slurry at 90°C.⁽⁷⁾ The following reactions were proposed to describe the reactions for hydronium jarosite, plumbojarosite and argentojarosite respectively:



[0007] After liberation, Ag was subsequently recoverable by cyanidation.⁽⁷⁾

[0008] Destruction of jarosites produced in pressure leaching at 85°C to 90°C using an approximately stoichiometric quantity of lime, followed by cyanidation, improved Ag recoveries from less than 5% to more than 97%.⁽⁹⁾

[0009] NaOH has also been used to facilitate alkaline decomposition of jarosite-type materials before cyanidation.⁽⁸⁾

[0010] Leaching of jarosite-containing materials in an acidic brine medium of CaCl_2 at a temperature above the boiling point of the solution and elevated pressures, in the presence of lime or another suitable alkali to maintain the pH between 1.5 and 3.5, has been proposed to recover metals from jarosite⁽⁶⁾. Although this method was successful to recover Ag and Pb from jarosites the use of high pressures and temperatures is not always desirable.

[0011] It seems obvious that if metal recovery from jarosites is required, an alkaline pretreatment followed by cyanidation is a generally accepted and suitable method. However, cyanide has environmental disadvantages, and in some cases, cyanide consumption is too high for such a process to be economical, particularly in the presence of base metals like Cu, and sulfides.

[0012] Also, it is implied that jarosite-containing materials can be pretreated in an alkaline medium to liberate certain metals and that, once the metals are in suitable forms, brine leaching can be used to solubilise them. However, this treatment implies the use of a liquid/solid separation step between the alkaline decomposition stage and the acidic brine solubilisation, and additional process steps and costs. There would be advantages to eliminating this liquid/solid separation, by carrying out the alkaline decomposition in a brine medium followed immediately by acidification to solubilise the required metals. Also, the alkaline decomposition step is shown to be facilitated in a brine solution.

SUMMARY OF INVENTION

[0013] The invention provides a method to dissolve at least one metal from jarosite or other iron hydroxy sulfate-containing material which includes the steps of:

- a) subjecting the material to alkaline treatment in a brine solution to facilitate jarosite decomposition, and
- b) acidification of the brine slurry to solubilise the liberated metal.

5 **[0014]** The method may include the step of adjusting the pH of the brine slurry to remove solubilised iron or other impurities from the slurry followed by the step of separating metal-containing brine solution and solid residue from each other.

10 **[0015]** The metal value or values can be removed from the brine solution by any appropriate means selected, for example, from: cementation, ion exchange, solvent extraction, electrowinning and precipitation. After metal recovery, the barren brine liquor may be recycled to the alkaline treatment stage. A bleed stream may be introduced to control impurities, and additional NaCl and water may be added on recycle to compensate for any losses. Preferably the temperature in the alkaline treatment stage is between 30°C and 100°C.

15 **[0016]** Alkali may added to the brine solution in the form of lime, NaOH, LiOH or any other suitable alkali, or any combination thereof.

[0017] Preferably the brine concentration is between 100 g/l NaCl and saturation levels, or the equivalent of any other soluble chloride salt.

20 **[0018]** The temperature in the acidic brine leach stage may be between 30°C and 100°C.

[0019] The pH of the acidic brine leach stage is preferably less than 6.

[0020] The method may be used particularly for the recovery of silver.

BRIEF DESCRIPTION OF THE DRAWING

25 **[0021]** The invention is further described by way of examples with reference to the accompanying drawing which is a flow chart representation of the method of the invention.

DESCRIPTION OF PREFERRED EMBODIMENT

30 **[0022]** Referring to the accompanying drawing, a silver and jarosite-containing residue (10) is typically obtained by subjecting a silver-bearing material to a leaching process (e.g. bioleaching or pressure leaching) or by subjecting a silver and iron containing liquor to a precipitation process (e.g. iron removal).

[0023] The residue is subjected to an alkaline pretreatment in a brine medium (12). The liquid to solid ratio should be sufficient to ensure ease of operation and to ensure that no solubility constraints exist for the silver. The brine solution or slurry should contain from 100 g/l NaCl to saturation levels, preferably 200 g/l to 300 g/l. The brine solution may contain various impurities, including sulfate. Sulfate levels of up to 10 g/l may be acceptable, but less than 5 g/l are expected if lime is used as the alkali. The slurry should be maintained at a temperature of 30°C to 100°C, preferably 50°C – 90°C.

[0024] An alkali (14), such as lime, is added to the slurry either to maintain an alkaline pH (>7), preferably greater than or equal to 9, and less than 13, or at a fixed addition rate based on the stoichiometry of the alkaline decomposition reaction.

[0025] The reaction is allowed to continue for a time depending on the composition of the material and the reaction temperature and pH. Usually a few hours are sufficient but more than 24 hours may be required in some cases, particularly in the lower pH or temperature ranges.

[0026] The alkaline brine slurry is then acidified (step 16), without any intermediate liquid/solid separation, by the addition of any suitable acid (18), preferably HCl or H₂SO₄, to a pH most suitable for the metal that is to be dissolved. For Ag, the pH should be greater than 0.1 and less than 6, preferably between 1 and 3.

[0027] The temperature of the acidic brine leach can be the same as that used in the alkaline pretreatment step (30°C – 100°C) and is preferably 70°C - 90°C.

[0028] As for the alkaline pretreatment stage, the residence time required for the acid leaching stage is variable, but is not expected to be longer than 8 hours.

[0029] An iron removal stage 20 may be included where the pH of the slurry is increased slightly by the addition of a suitable alkali 22, to precipitate iron. The pH should be less than 5.

[0030] After liquid/solid separation (24) to remove the solid residue 26, Ag is recovered by any suitable means, in this case, cementation 28 with Fe scrap

30. The Ag product is removed by liquid/solid separation (34) and the barren brine solution 36 is recycled to the alkaline pretreatment step (12).

[0031] Part of the brine solution 36 may be removed as a bleed stream 38 to control impurity build up. Also it may be necessary to add NaCl (40) and water 42 to make up the stream recycled to the stage 12.

Example 1

[0032] A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 80°C at a liquid to solid ratio of 10:1. The natural pH of the slurry ranged between 1.8 and 2.4. After leaching for 6 hours, the Ag dissolution was 22%.

[0033] This indicates that brine leaching alone is not sufficient to recover Ag from jarosite-type materials.

Example 2

[0034] A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to 145 kg Ca(OH)₂ per ton of sample, based on a stoichiometric excess of 20%, and the slurry was agitated for 2 hours. The slurry was then acidified to pH 2 by adding 97 kg H₂SO₄ per ton of sample, and agitated for a further 5 hours. Ag dissolution of 94% was obtained.

[0035] This illustrates the process of the invention using a fixed amount of alkali.

Example 3

[0036] A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 80°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9. After 3 hours, 126 kg Ca(OH)₂ per ton of sample had been consumed. The slurry was then acidified to pH 2 by adding 87 kg H₂SO₄ per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 93% was achieved.

[0037] This illustrates the process of the invention using a set pH during the alkali treatment.

Example 4

[0038] A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9.5. After 4 hours, 181 kg Ca(OH)₂ per ton of sample had been consumed. The slurry was then acidified to pH 2 by adding 100 kg H₂SO₄ per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 94% was achieved.

[0039] This test was repeated, but excluding brine from the alkaline decomposition stage. After 24 hours, 83 kg Ca(OH)₂ per ton of sample had been consumed. The slurry was then acidified by adding 54 kg H₂SO₄ per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 43% was achieved.

[0040] This illustrates that the presence of brine in the alkaline decomposition stage facilitates the decomposition of jarosite.

Example 5

[0041] A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to 145 kg Ca(OH)₂ per ton of sample, based on a stoichiometric excess of 20%, and the slurry was agitated for 2 hours. The slurry was then acidified to pH 2 by adding 131 kg H₂SO₄ per ton of sample, and agitated for a further 5 hours.

[0042] To remove Fe from the circuit, limestone was added as a solid to establish a pH of 3.7. The solid residue was then separated from the brine solution. Overall Ag dissolution of 87% was obtained.

[0043] This illustrates the process of the invention when an iron removal stage is included.

Example 6

[0044] The same procedure was carried out as for example 2, except that the temperature during alkaline pretreatment was 50°C, not 70°C. Acid consumption in the acid leach step was 164 kg H₂SO₄ per ton, and Ag dissolution was only 63%.

[0045] This example illustrates the importance of temperature in the alkaline treatment stage.

Example 7

[0046] A residue containing about 70% of Ag in jarosite was slurried with a 260 g/l NaCl solution at (a) 70°C and (b) 80°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9 for both tests, and the slurry was agitated until no further lime additions were necessary to maintain the set pH. The slurries were then acidified to pH 2 by adding (a) 82 and (b) 87 kg H₂SO₄ per ton of sample respectively, and agitated for a further 5 hours.

[0047] In both cases, Ag dissolution was 93%. However, where the alkali treatment was done at 70°C, 7.5 hours were required to complete this stage, while at 80°C, only 3 hours were required.

[0048] This example illustrates the effect of temperature and time on the proposed process.

REFERENCES

1. Raghavan R, Mohanan PK, Swarnkar SR, 'Hydrometallurgical processing of lead-bearing materials for the recovery of lead and silver as lead concentrate and lead metal', Hydrometallurgy 58, 2000, p103-116.
2. Gallagher NP, Lei KPV, 'Recovery of lead and silver from plumbojarostie by hydrothermal sulfidation and chloride leaching', Report of Investigations 9277, US Department of the Interior, Bureau of Mines.
3. Sandberg RG, Huiatt JL, 'Recovery of silver, gold, and lead from a complex sulphate ore using ferric chloride, thiourea, and brine leach solutions', Report of Investigations 9022, US Department of the Interior, Bureau of Mines.
4. Bahr A, Proesemann T, 'Recovery of silver from refractory ores', XVI International Mineral Processing Congress, Stockholm, June 5-10, 1988, Part B. E Forssberg (Ed.).
5. Martin D, Diaz G, 'Hydrometallurgical treatment of lead secondaries and/or low grade concentrates: the Placid and Ledclor processes', Conference: Recycling lead and zinc – the challenge of the 1990's, Rome 11-13 June 1991, International Lead and Zinc Study Group.
6. Peters MA, Hazen WW, Reynolds JE, 'Process for recovering metal values from jarosite solids', US Patent 5078786, 7 January 1992.

7. Berezowsky RMGS, Stiksmas J, Kerfoot DGE, Krysa BD, ' Silver and gold recovery from zinc pressure leach residue', Lead-Zinc '90, TS Mackey and RD Prengaman (Eds.), The Minerals, Metals and Materials Society, 1990.
8. Patino F, Salinas E, Cruells M, Roca A, ' Alkaline decomposition-cyanidation kinetics of argentian natrojarosite', Hydrometallurgy 49, 1998, p323-336.
9. Thompson P, Diaz M, Plenge G, 'Pressure oxidation of silver-bearing sulphate flotation concentrates', Mining Eng., September 1993, p1195-1200.